NAS 1.26:3307

THE MULTISTATE IMPACT PARAMETER METHOD FOR MOLECULAR CHARGE EXCHANGE IN NITROGEN... NASA CONTRACTOR RPT. 3307... SCIENTIFIC AND TECHNICAL INFORMATION BRANCH, NATIONAL AERONAUTICS & SPACE ADMINISTRATION... 1980

1 OF 1
24X
SUPTDOCS
GPO

CONTENTS

	Page	
LIST OF FIGURES	iv	1/A6
SUMMARY	1	1/A7
I. INTRODUCTION	2	1/A8
II. THEORY OF CHARGE EXCHANGE	4	1/A10
III. CROSS SECTIONS	12	1/B4
IV. COLLISION TIMES	23	1/C4
V. DECAY OF EXCITED STATES OF N_2^+	24	1/C5
REFERENCES	26	1/C7

Item 830-H-14 NAS 1.26 : 3307

AUG 2 2 1980

COMPLETED

ORIGINAL

NASA Contractor Report 3307

The Multistate Impact Parameter Method for Molecular Charge Exchange in Nitrogen

Juliette W. Ioup

GRANT NSG-1361
AUGUST 1980

NASA

34

NASA Contractor Report 3307

The Multistate Impact Parameter Method for Molecular Charge Exchange in Nitrogen

Juliette W. Ioup
Xavier University
New Orleans, Louisiana

Prepared for
Langley Research Center
under Grant NSG-1361

National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1980

Blank Page

CONTENTS

	Page
LIST OF FIGURES	iv
SUMMARY	1
I. INTRODUCTION	2
II. THEORY OF CHARGE EXCHANGE	4
III. CROSS SECTIONS	12
IV. COLLISION TIMES	23
V. DECAY OF EXCITED STATES OF N_2^+	24
REFERENCES	26

LIST OF FIGURES

Fig. 1. Impact parameter collision model. 6

Fig. 2. Schematic diagram of the total experimental system showing the mass spectrometer section, ion-optics section, and the charge-transfer section. 13

Fig. 3. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 16 eV. 15

Fig. 4. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 17.5 eV. 15

Fig. 5. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 19.5 eV. 16

Fig. 6. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 0.99×10^{-4} torr 16

Fig. 7. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.33×10^{-4} torr 17

Fig. 8. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.66×10^{-4} torr 17

Fig. 9. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.987×10^{-4} torr 18

Fig.10. Comparison of total charge transfer cross sections from Smith with selected experimental data from the literature. 20

Fig.11. Comparison of total charge transfer cross sections from Smith with selected theoretical calculations from the literature . . . 21

SUMMARY

The multistate impact parameter method of Flannery *et al.* is applied to the calculation of total cross sections for low-energy charge transfer between nitrogen ions and nitrogen molecules. Experimental data showing the relationships between total cross section and ion energy for various pressures and electron ionization energies were obtained by Smith at NASA Langley Research Center. Calculated and experimental cross section values from this work are compared with the experimental and theoretical results of other investigators.

I. INTRODUCTION

In recent years, a number of experimental and theoretical investigations have involved the study of reactions of charged and neutral atmospheric species.[1-18] Nevertheless, a detailed understanding of many atmospheric phenomena is not known, due to a lack of precise experimental information concerning the discrete atomic and molecular processes involved.

Many satellite and reentry probe experiments have encountered serious measurement problems with atomic and molecular atmospheric gases.[19-21] Data on gas - gas collisions is required at temperatures much above those at which viscosity, thermal conductivity, diffusivity, and mobilities can be directly measured. Space flight experiments at Mach numbers above 8 correspond to interaction energies (between the vehicle and atmospheric gases) of more than 1 eV. Satellite and missile velocities correspond to interaction energies in the vicinity of 10 eV for nitrogen molecules. The activation energies for many common chemical reactions lie between 1 and 4 eV. Chemical bond strengths are on the order of 8 eV. Collision processes offer a means for investigating these bond strengths. Considerable basic scientific interest derives from the use of gas-gas collision experiments for the inference of intermolecular potentials because accurate calculations for intermolecular potentials are difficult or impossible to obtain. Collision experiments also play an important role in providing information on systems not amenable to theoretical investigation as well as for comparison to approximations which are available.

The reactions chosen for study were symmetric charge transfer between N_2^+ and N_2. Nitrogen was chosen partly because of its prevalence in atmospheric experiments; it can readily be used as a calibration system. The following reactions were considered:

$$N_2^+(X^2\Sigma_g^+, \nu_o') + N_2(X^1\Sigma_g^+, \nu_o'') \rightarrow$$

$$N_2^+(X^2\Sigma_g^+, \nu') + N_2(X^1\Sigma_g^+, \nu'')$$

$$N_2^+(A^2\pi_u, \nu_o') + N_2(X^1\Sigma_g^+, \nu_o'') \rightarrow$$

$$N_2^+(A^2\pi_u, \nu') + N_2(X^1\Sigma_g^+, \nu'')$$

$$N_2^+(B^2\Sigma_u^+, \nu_o') + N_2(X^1\Sigma_g^+, \nu_o'') \rightarrow$$

$$N_2^+(B^2\Sigma_u^+, \nu') + N_2(X^1\Sigma_g^+, \nu'')$$

Relative translational energies of interest were in the range from 9 to 441 eV. Since the target gas possesses only thermal energy, the relative energy was effectively that of the ion beam. Three particular states of N_2^+ were of interest: $X^2\Sigma_g^+$, $A^2\pi_u$, and $B^2\Sigma_u^+$ have formation thresholds which occur at electron energies of 15.63, 17.0, and 18.94 eV, respectively.[22]

The author gratefully acknowledges the assistance of Alphonso C. Smith, Instrument Research Division, NASA Langley Research Center, for the use of data acquired with his experimental apparatus and for many helpful discussions.

II. THEORY OF CHARGE EXCHANGE

Comparatively little detailed theoretical work has been done on the collision of a molecular ion with its neutral parent. The treatment is more complicated than the atomic case because vibrational excitation may result from the nuclear potential energy changes which occur with charge transfer. Bates and Reid[23] formulated and applied a theoretical treatment of molecular charge transfer in which specific account is taken of the important coupling not acknowledged by the usual two-state treatment of Gurnee and Magee.[16] The most recent treatment of molecular charge transfer is given by the full multistate impact parameter treatment of Flannery, Cosby, and Moran.[12]

In the theoretical studies of charge transfer, as in theoretical studies of other types of collision between atomic systems, there are two main approximations: a high velocity approximation in which the perturbation causing the transition is taken to be the interaction potential, and a low velocity approximation in which the pertubation is taken to be the relative motion. Since the present work was accomplished in the low velocity range, the perturbation was taken to be the relative velocity. The present discussion will outline the multistate impact parameter treatment of reference 12. This method attempts to take into account the vibrational states of the incident ions and of the products, while the target neutral molecules are assumed to be in the ground state.

When the charge-transfer process for diatomic nitrogen is resonant and symmetric, the wave function $\Psi(t)$ for internal motion may be expanded in terms of the gerade and ungerade eigenfunctions $X_{g,u}(\vec{r}, \vec{R})$ for each electronic state of the quasimolecular complex formed. The atomic separation in the molecule is $\vec{r}$

and the distance between the two centers of mass is $\vec{R}$. The relative phase η changes with $\vec{R}$ because of differences in eigenenergies $E_{g,u}(\vec{R})$. Bates and Lynn[24] point out that charge transfer does not occur because of an electronic transition but because of a phase change. The impact parameter model used to calculate the charge-transfer cross sections is shown in Figure 1. In this model, the initial state of the molecule is at the point a, located at a distance $\vec{\rho}$ from the Z axis, and the ion is at the point b, which is located at $Z = -\infty$. The point b moves along the Z axis with the constant velocity $\vec{v}$. In the final state the ion is at point a and the molecule at the point b, where b is now located at $Z = +\infty$. A straight line trajectory is assumed where $\vec{\rho}$ is the impact parameter and v is the incident speed along the Z-axis, and $\vec{R} = \vec{\rho} + \vec{v}t$. The probability for symmetrical resonant charge transfer as determined from a two-state (gerade-ungerade) molecule treatment (in which the coupled equation can be solved exactly) is given as:[23]

$$P_M^+(\rho) = \sin^2 \eta(\rho) \tag{1}$$

where

$$\eta(\rho) = \frac{1}{\hbar v} \int_0^{+\infty} [\varepsilon_g(R) - \varepsilon_u(R)]\, dZ \tag{2}$$

The charge-transfer cross section is then given as

$$\sigma = 2\pi \int_0^{+\infty} \rho \sin^2 \eta(\rho) d\rho \tag{3}$$

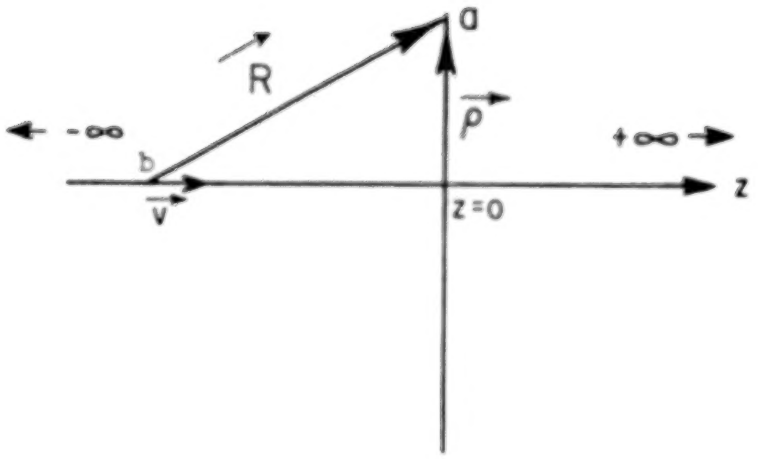


Fig. 1. Impact parameter collision model.

In order to include nonresonant channels, the wave function is expanded[23] in terms of $\phi_n^\alpha(\vec{r})$, the molecular eigenfunctions of the unperturbed Hamiltonian for the isolated molecular systems. The $\phi_n^\alpha(\vec{r})$ have electronic, vibrational, and rotational parts. The eigenenergies at infinite center-of-mass separation are E_n^α, and

$$\Psi(t) = \sum_{\alpha=D,X} \sum_n a_n^\alpha \phi_n^\alpha(\vec{r}) \exp(-iE_n^\alpha t/n) \qquad (4)$$

The index α refers to either the direct D (no charge transfer) or to the exchange channels X. Bates and Reid[23] used the expanded form of equation (4), substituted it into the time-dependent Schrodinger equation for internal coordinates, and derived the following relation for charge-transfer cross section to lowest order:

$$\sigma = 2\pi \int_0^{+\infty} |C_f^X(\rho, \infty)|^2 \rho d\rho \qquad (5)$$

The transition amplitudes $C_f^X(\rho, t)$ are the solutions to the set of first order coupled differential equations

$$i \frac{\partial C_\ell^\alpha}{\partial} = V(R) \sum_{m=1}^{N} P_{\ell m} C_m^{\bar{\alpha}}(\rho, t) \exp i(E_\ell - E_m)t/n, \quad \ell = 1, 2, \cdots N \qquad (6)$$

where $\bar{\alpha}$ = X when α = D and vice versa. Only the direct channel i is occupied initially, therefore:

$$C_m^D(\rho, -\infty) = \delta_{mi}$$
$$C_m^X(\rho, -\infty) = 0 \tag{7}$$

The matrix elements $P_{\ell m}$ are

$$P_{\ell m} = F(v_\ell', v_m'') \; F(v_m', v_\ell'') \tag{8}$$

where $F(v_i', v_n'')$ is the vibrational overlap of the incident ion in the v_i' vibrational state and the target neutral in the v_n'' vibrational state. The rotational motion is neglected since the rotational times are much greater than the collision times,[12] i.e., the collision is finished before the molecular complex can rotate significantly. The interaction potential V(R) is assumed to be spherically symmetric and can be obtained from the gerade-ungerade splitting of the vibrational motion[12] as

$$V(R) = \frac{1}{2} \left[\epsilon_g(R) - \epsilon_u(R)\right] \tag{9}$$

Then the exchange cross section becomes

$$\sigma = 2\pi \int_0^{+\infty} \rho \sin^2 \left[\frac{2}{\hbar v} \int_0^{+\infty} V(R) \, dz \right] \tag{10}$$

The gerade potential is given by the Morse function[25] as

$$\varepsilon_g(R) = D_e [\exp(-2\beta(R - R_e)) - 2\exp(-\beta(R - R_e))] \qquad (11)$$

where R_e is the internuclear distance corresponding to the potential minimum of depth D_e, and β describes the shape of the potential. The modified Lennard-Jones potential,[26-27]

$$V_{LJ4} = 4\varepsilon \left[\left(\frac{d}{R}\right)^{12} - \left(\frac{d}{R}\right)^{6}\right] - \frac{\alpha e^2}{2R^4} \qquad (12)$$

where α is the polarizability and ε and d are Lennard-Jones parameters which are known for the nitrogen potential,[28] gives the interaction energy for the gerade state for this reaction. Fitting the Morse curve to the modified Lennard-Jones potential allows determination of the parameters $R_e = 3.5262 \times 10^{-8}$ cm, $D_e = 0.06917$ eV and $\beta = 1.5903 \times 10^{-8}$ cm^{-1} for nitrogen.[12]

Sato[29] proposed that the ungerade potential may be written as

$$\varepsilon_u(R) = \tfrac{1}{2}D_e [\exp(-2\beta(R - R_e)) + 2\exp(-\beta(R - R_e))] \qquad (13)$$

The interaction potential V(R) for equation (9) is therefore found to be

$$V(R) = \begin{cases} \tfrac{1}{4}D_e \exp(-2\beta(R - R_e)) - \tfrac{3}{2}D_e \exp(-\beta(R - R_e)) & R > R^* \\ 0 & R < R^* \end{cases} \qquad (14)$$

$V(R)$ is set equal to zero for small $R < R^*$, where $R^* = R_e - \ln 6/\beta = 2.3995 \times 10^{-8}$cm for N_4^+, since negative values of the interaction potential are unphysical. Since D_e, R_e, and β have determined, the interaction potential is now known.

Vibrational overlaps are needed in order to obtain the transition amplitude C_f^x for the charge-transfer cross section in equation (5). Overlaps for diatomic ions and neutral molecules in the ground state are given by Nicholls.[30] Flannery et al.[12] computed overlaps for excited states of the neutral using Frank-Condon factors[30] with a Morse anharmonic oscillator wavefunction.[30,31] The excitation defects of various reaction channels were computed from spectroscopic energy levels[25,32,33] of the ionic and neutral species. They found[12] that the excitation defects occurred in groups or "bands" separated by approximately one vibrational quantum of energy, about 0.25 eV.[34] Therefore the channels could be considered to be degenerate within a given band, greatly simplifying the calculations involved. The transition probabilities $P_{\ell m} = |C_f^x|^2$ were obtained as a function of impact parameter ρ by solving the multistate equations (6) numerically by the Adams-Moulton method.[35] The charge transfer cross sections σ were obtained from equation (5) using these transition probabilities by numerical integration over impact parameter using Simpson's rule with a built-in accuracy parameter.

The low-velocity approximation[23] can be used for collisions in which the incident velocity is small enough so that the excitation defect $E_\ell - E_m$ is approximately zero. Then equations (6) for the transition probability become

$$\frac{i\partial C_\ell^\alpha}{\partial t} = V(R) \sum_{m=1}^{B} P_{\ell m} C_m^{\bar{\alpha}}(\rho,t), \quad \ell = 1,2,3\ldots B \tag{15}$$

where B is the number of degenerate final states which have zero energy defect with respect to the incident energies. The exchange cross section then becomes

$$\sigma = 2\pi \sum_{n=1}^{B} X_{in}^2 \int_0^{+\infty} \rho \sin^2 \left[\frac{\pi_n}{nv} \int_{-\infty}^{+\infty} V(R) \, dz \right] d\rho \qquad (16)$$

where the π_n are the eigenvalues and X_{in} the associated eigenfunctions of the matrix which diagonalizes the matrix P formed from the $P_{\ell m}$; that is

$$\Pi = X^{-1} PX = \tilde{X} PX \qquad (17)$$

III. CROSS SECTIONS

The NASA-Langley experimental system designed and built by Smith[36] can be divided for the purpose of discussion into three component parts: a mass-spectrometer, an ion-optics section, and a charge-transfer section, as shown in Figure 2.

The purpose of the mass spectrometer was to provide a mass-selected primary-ion beam with known kinetic energy. The mass spectrometer system contained an electron-bombardment ion source, a gas inlet system, a vacuum pumping station, a pressure monitoring system and electronic controls.

The purpose of the ion-optics section was to direct and guide the transport of the primary ion beam from the mass spectrometer analyzer exit at the ring-drawout electrode to the charge-transfer cell (CTC). This was done by employing conventional ion optic techniques with lens elements that were of three basic geometric configurations: cylindrical, disc, and flat plate type. The electrical potentials on all optical elements were separately controlled by regulated power supplies to obtain a stable ion beam of maximum intensity at the CTC section.

The charge-transfer cell section consisted of three parts: The charge transfer cell, the charge-transfer-cell screen, and beam flag two. This section was utilized to detect and measure the primary and product ions made in the charge transfer process. Detection of the ion beam was done by absolute current measurement using three precision electrometers to measure the total currents. Exact control of the primary-ion states was not possible with the normal electron impact ionization ion source. However, some control in specific state population was possible by selecting the electron ionization energy to correspond to the threshold of a specific electronic state.

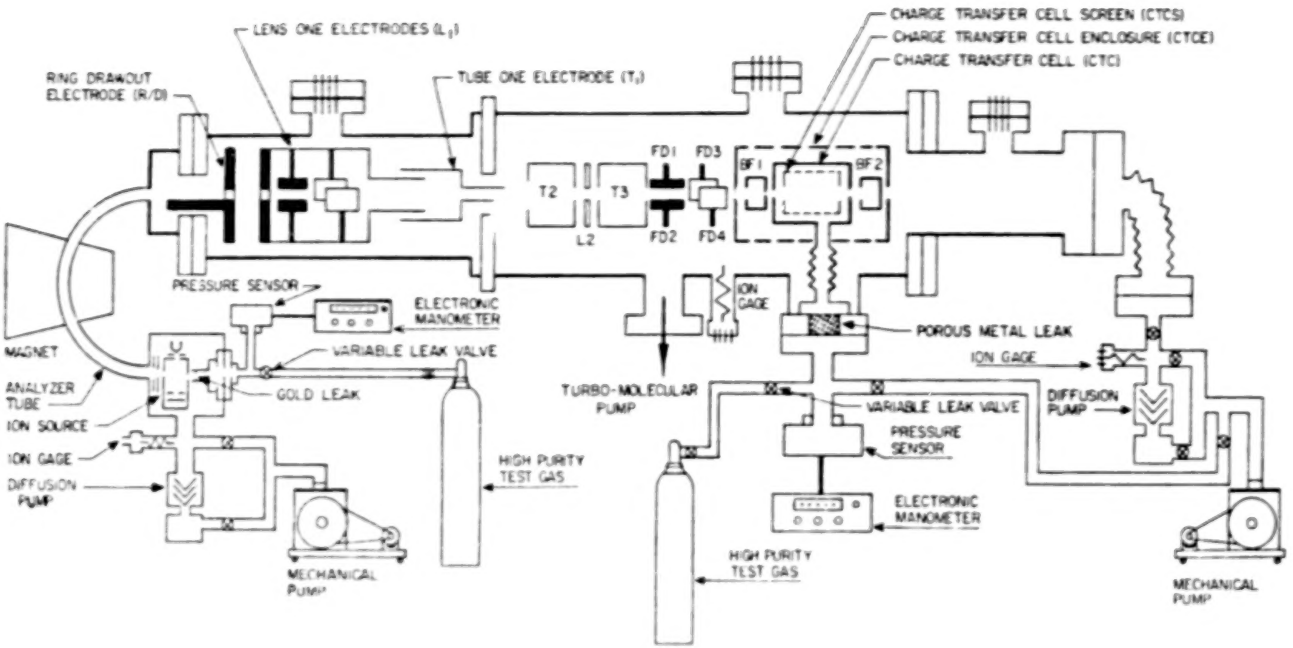


Fig. 2. Schematic diagram of the total experimental system showing the mass spectrometer section, ion-optics section, and the charge-transfer section.

The apparatus was maintained in the 10^{-6} torr pressure range by the use of three separate pumping stations. The volume enclosing the mass spectrometer, the lens one optic section, and the first tube electrode was maintained at working pressures of 2-4 x 10^{-6} torr by a 2-inch, 80-liter-per-second oil diffusion pump and mechanical pump arrangement. The middle volume was maintained at working pressures of 5 x 10^{-7} to 5 x 10^{-6} torr using a 400-liter-per-second turbo-molecular pump. Another 2-inch, 80 liter-per-second oil-diffusion and mechanical-pumping station was used to help evacuate the volume at the exit of the charge transfer cell. A detailed description of the experimental apparatus has been given elsewhere.[36,37]

Figures 3-5 present total charge-transfer cross sections for N_2^+ on N_2 obtained at different pressures in the charge transfer cell as a function of the square root of the incident ion kinetic energy. Each figure contains data points obtained at pressures in the CTC of 0.99, 1.33, 1.66, and 1.987 x 10^{-4} torr. Figure 3 shows cross sections obtained for ionizing electron energy of 16 eV, Figure 4 for electron energy 17.5 eV, and Figure 5 for electron energy 19.5 eV.

Figures 6-9 show the same data of total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of incident ion kinetic energy. Each plot contains data for the three different ionizing electron energies (16.0, 17.5, and 19.5 eV) with a separate figure for each different pressure in the CTC.

In Figure 10 we have plotted the Langley data for comparison with the experimental results of others from the literature. Ghosh and Sheridan[38] (GS) stated that their data included N_2^+ ions in the ground state when leaving their Heil-type ion source. The pressure in their collision chamber was measured by a Knudsen gauge to be 17 x 10^{-5} torr. The electron energy in the ion source of

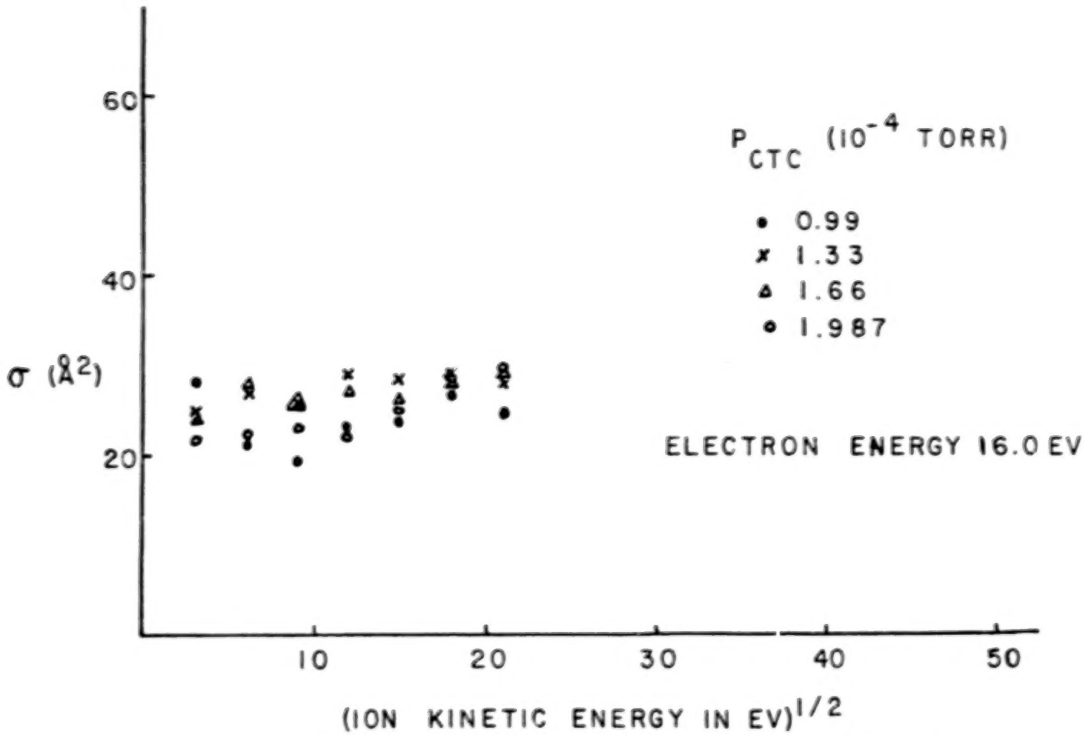


Fig. 3. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 16 eV.

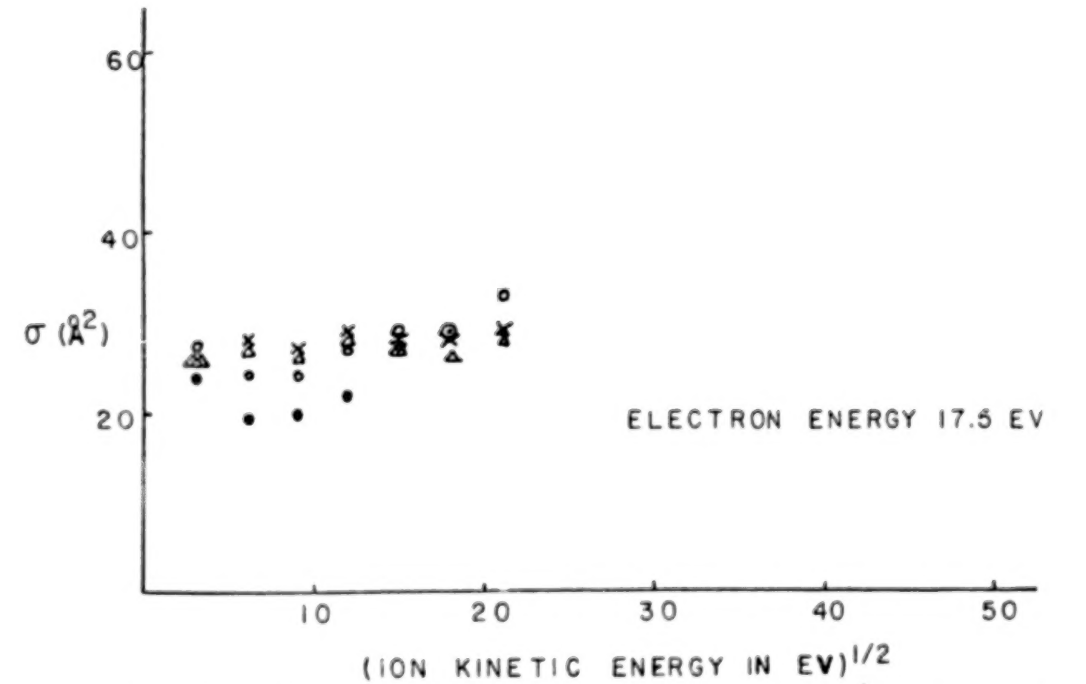


Fig. 4. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 17.5 eV.

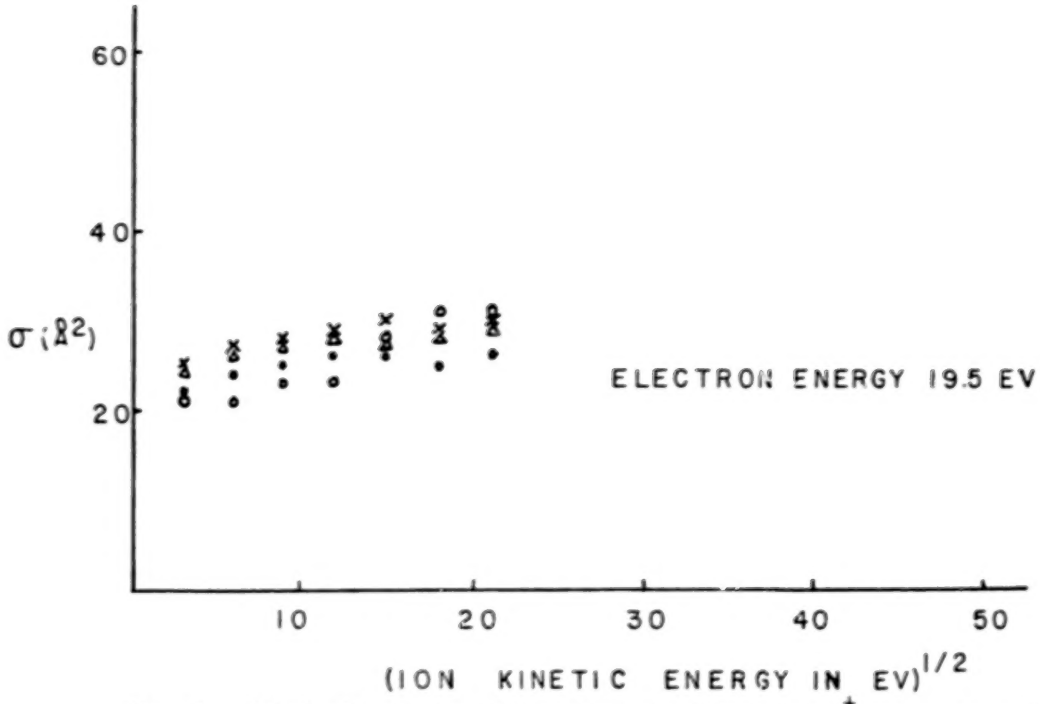


Fig. 5. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various pressures in the charge-transfer cell, with ionizing electron energy of 19.5 eV.

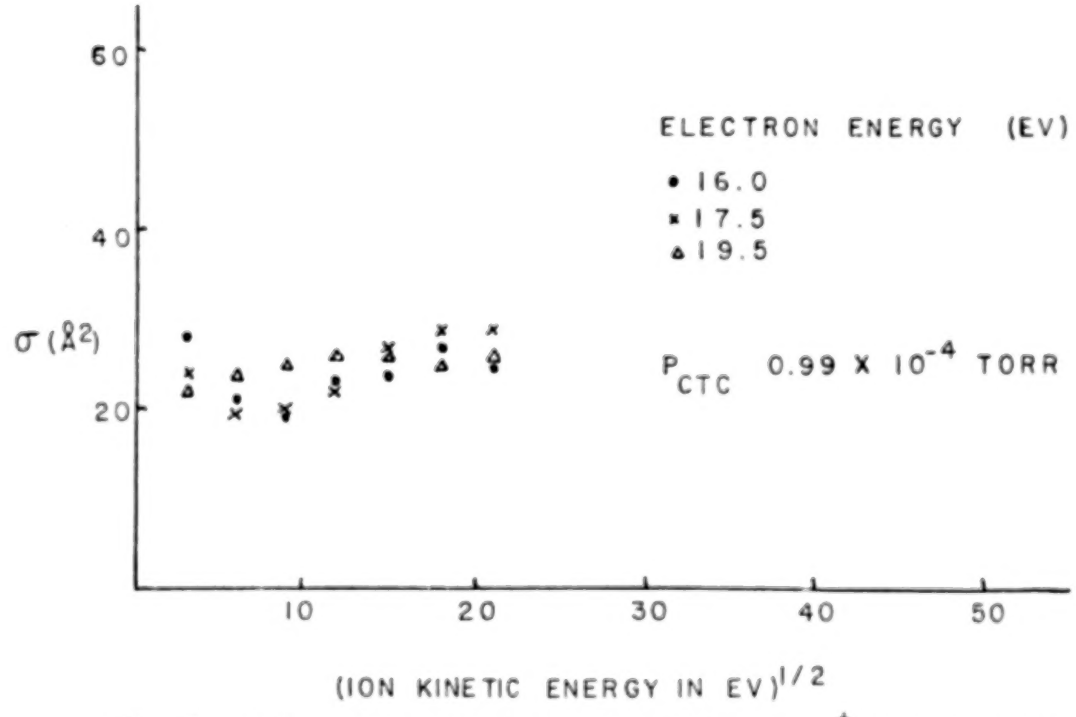


Fig. 6. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 0.99×10^{-4} torr.

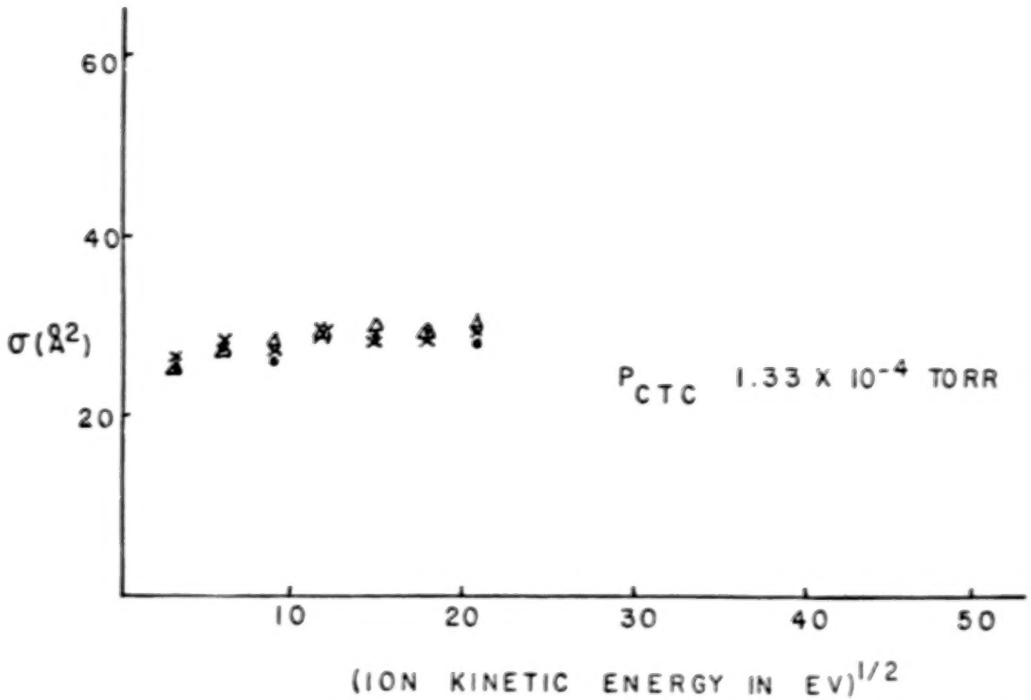


Fig. 7. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.33×10^{-4} torr.

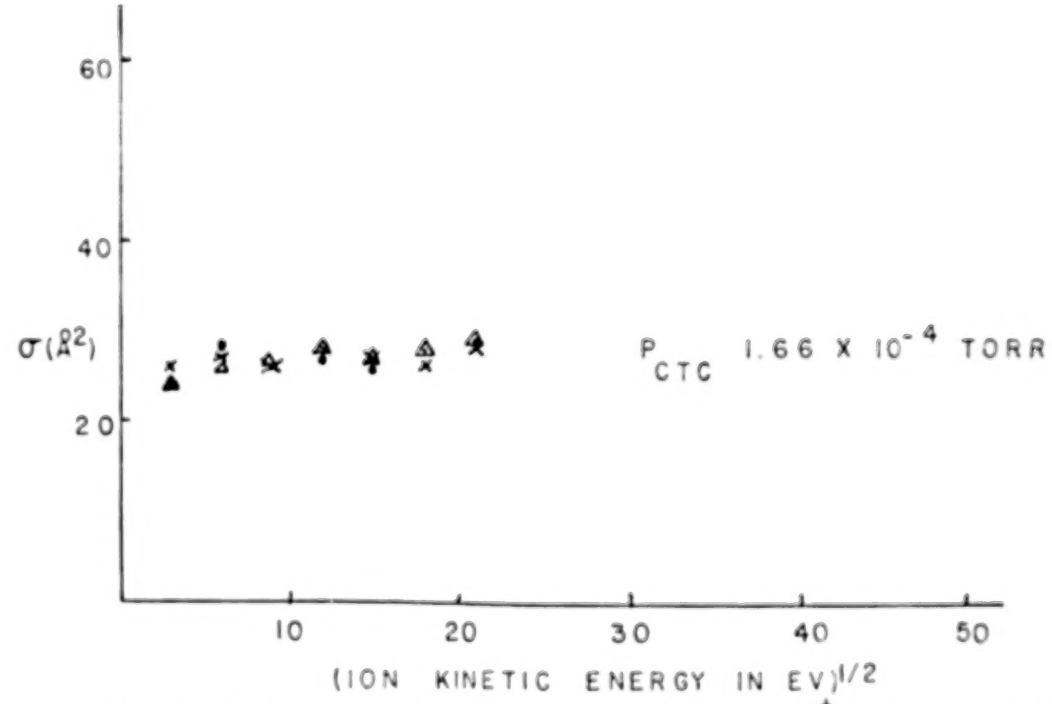


Fig. 8. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.66×10^{-4} torr.

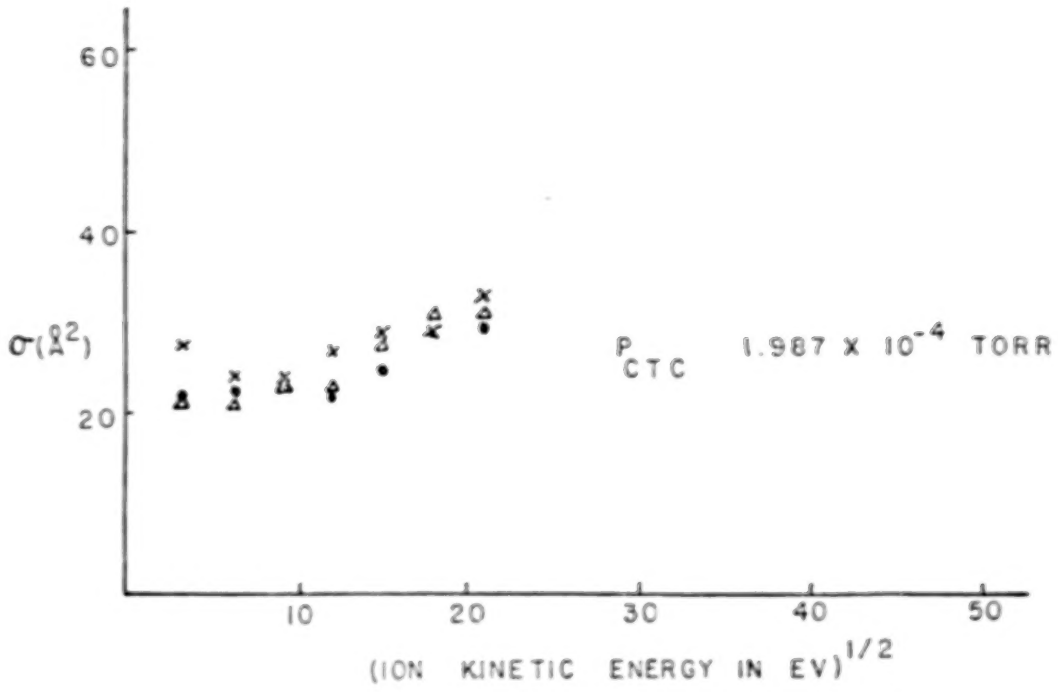


Fig. 9. Total charge-transfer cross sections for N_2^+ on N_2 as a function of the square root of the incident ion kinetic energy for various ionizing electron energies, with pressure in the charge-transfer cell of 1.987×10^{-4} torr.

Stebbings, Turner, and Smith[3] (STS) was 200 eV. Nichols and Witteborn[10] (NW) measured cross sections at very low ion energies of less than 17 eV. The electron energy in their ion source was 95 eV, and their reaction chamber pressure was varied between 0.1 and 80 x 10^{-5} torr. Lehrle et al.[2] (LPRS) studied charge transfer cross sections for an electron energy of 25 eV and a collision pressure of 2 x 10^{-5} torr, measured by a Bendix gauge. Homer et al.[6] (HLRT) obtained their data using 70 eV of electron energy and collision pressures not quoted. Gustafsson and Lindholm[39] (GL) data were taken for a collision pressure of 17 x 10^{-5} torr but the electron energy was not given. Utterback and Miller[1] (UM) used 22 eV electrons in their ion source and the pressure in their collision region was 20 x 10^{-5} torr. Potter[11] (P) claims to have only ground state ions in his incident beam, although this is doubtful since his ion source was operated at 75 eV. In the experimental results of Leventhal et al.[13] (LMF) no information was given about the electron energy of the collision chamber pressure.

In Figure 11 a comparison of Smith's results is made with theoretical calculations of Flannery et al.[12] and Leventhal et al.[13]. The full multistate treatment and low velocity approximation were calculated by Flannery et al. using the distribution of vibration levels in the incident ion beam corresponding to an electron excitation energy of 22 eV. Additional calculated cross sections obtained by Leventhal et al.[13] using the impact parameter method are also shown in Figure 11. The results of Moran et al.[14] are shown, where they obtained much lower values of cross sections using the multistate impact parameter method[12] to obtain data for individual channels and integral cross sections summed over all product channels. Theoretical cross sections were obtained as a function of the square root of incident ion kinetic energy for nitrogen when both incident ion target neutrals were in the ground electronic and vibrational state and

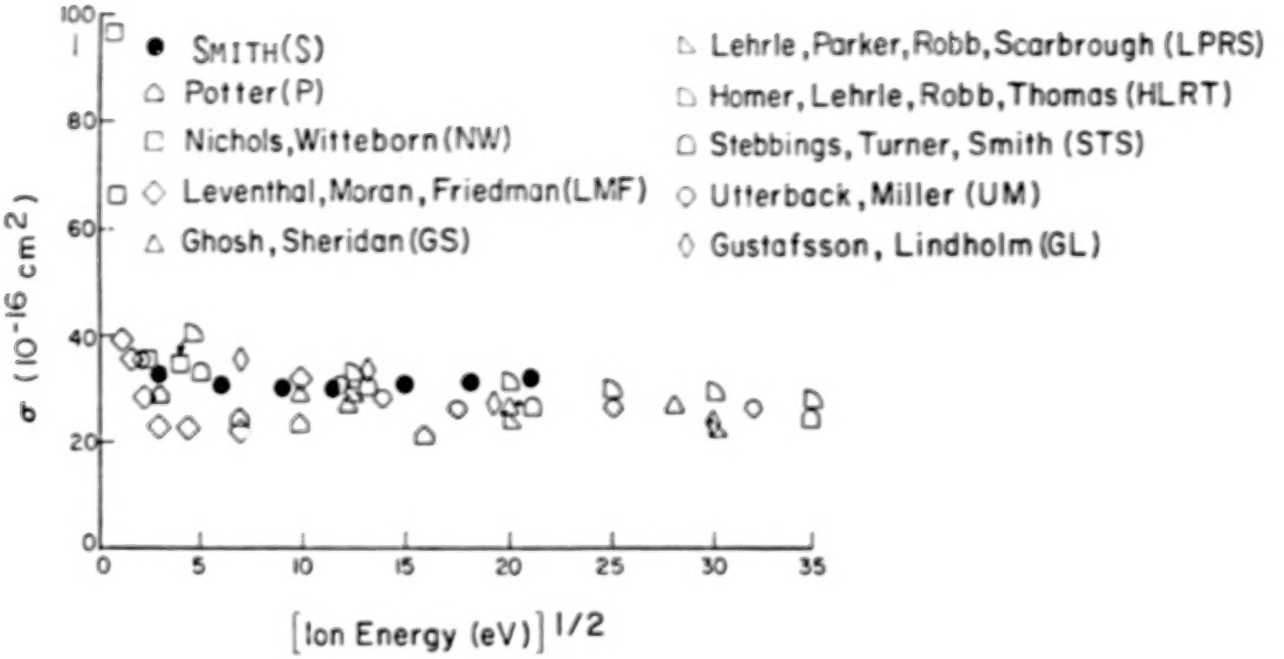


Fig. 10. Comparison of total charge-transfer cross sections from Smith with selected experimental data from the literature.

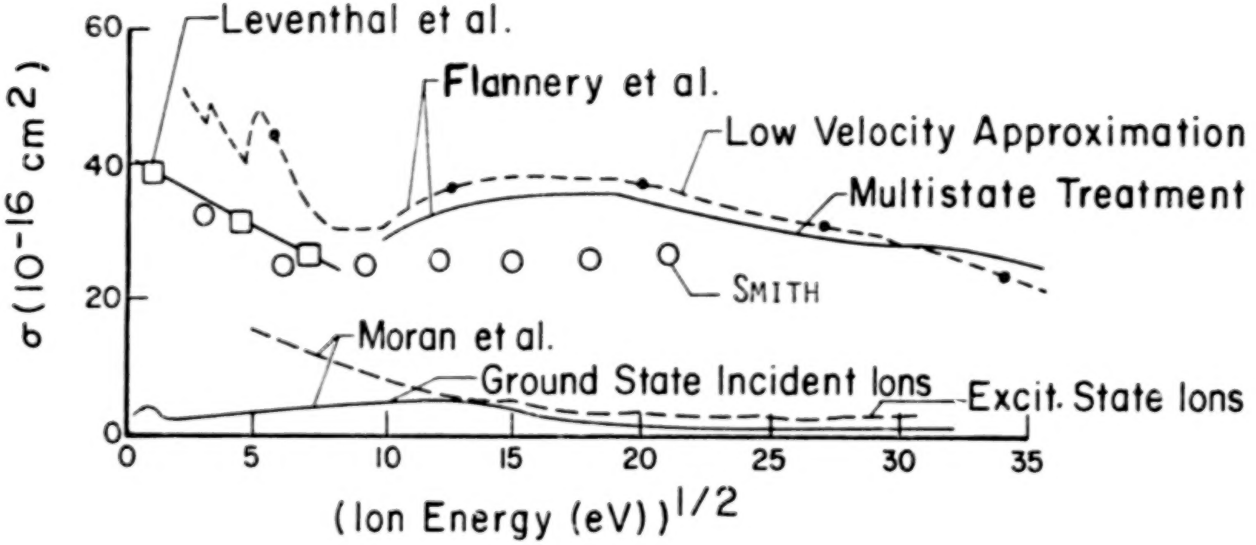


Fig. 11. Comparison of total charge-transfer cross sections from Smith with selected theoretical calculations from the literature.

the resultant product neutrals and ions in vibrational states (ν,ν') equal to (0, 1), (1, 0), and (0, 2) for the excitation products. Moran *et al.* obtained theoretical cross sections for total vibration excitation with the incident ion in the ground electronic state $N_2^+(X^2\ \Sigma_g^+)$ and vibrational state 0, 1, 2, 3, with the target neutral in the ground electronic and vibrational state $N_2(X^1\ \Sigma_g^+,\ \nu = 0)$ as a function of incident ion kinetic energy. The cross sections obtained were less than $10 \times 10^{-16} cm^2$ for incident ion energies larger than about 75 eV.

IV. COLLISION TIMES

Electronic, vibrational and rotational transitions will be important only when such transitions can take place during the time of the collision. The vibrational and rotational periods of N_2 are $\tau_{vib} \sim 2 \times 10^{-14}$ sec and $\tau_{rot} \sim 2 \times 10^{-12}$ sec.[12] The collision time, i.e., the lifetime of the ion-molecule complex, is $\tau_{coll} \sim 2.4(R/v)10^{-17}$ sec in atomic units.[12] The range of incident energies, 9 eV < E < 441 eV, or speeds, $5 \times 10^{-3} < v < 4 \times 10^{-2}$ (in atomic units), in the Langley collision experiment is the same order of magnitude as the speed range of $7 \times 10^{-3} < v < 6 \times 10^{-2}$ given by Flannery et al.[12] These speeds involve large interaction radii $10 > R > 5$ for the collision. Then the collision times are in the range 4.7×10^{-14} sec $> \tau_{coll} > 3.4 \times 10^{-15}$ sec. Therefore the collision times are much much less than the time of rotation, and the collision is finished before the ion-molecule complex can rotate significantly. However, the collision time is the same order of magnitude as the vibrational time, and a vibrational transition is highly likely during the collision.

V. DECAY OF EXCITED STATES OF N_2^+

For the measurement of total charge-transfer cross sections, consideration should be given to the lifetimes for the existence of the various excited states of N_2^+. The length of the Langley charge-transfer cell is 5.0419 cm. For an ion of incident energy 9 eV, or incident speed 7.87×10^5 cm/sec, the time spent in the CTC is on the order of 6.41 microseconds; for an ion of incident energy 441 eV, incident speed 5.51×10^6 cm/sec, the time is of order 0.915 microsecond. Since the electron energies to produce the N_2^+ were selected to be between 11.6 and 32.1 eV in the Langley experiment, only the ground state N_2^+ ($X^2 \Sigma_g^+$) and the first two excited states, N_2^+ ($A^2 \pi_u$) and N_2^+ ($B^2 \Sigma_u^+$) need to be considered. The lifetimes of B → X radiative transitions are on the order of 60 nanosecond,[40,41] so that all the N_2^+ ($B^2 \Sigma_u^+$) ions formed in the electron impact ionization undergo transitions to the ground state N_2^+ ($X^2 \Sigma_g^+$) long before they arrive at the CTC region. The lifetimes of the A → X radiative transitions are on the order of 5-15 microseconds for the first few vibrational levels.[42-44] These ions undergo transitions which occur exponentially with distance as $e^{-t/\tau}$ where τ is given in the following table for the first few vibrational levels.[42] For typical collision experiments, the ion transit times are on the order of 10 to 12 microseconds. For these transit times, some undecayed $N_2^+(A^2 \pi_u)$ excited states will be present in the ion beam. The presence of some undecayed $N_2^+(A^2 \pi_u)$ states was included by Flannery et al.[12] since the ions were contained for 9.6 - 14.2 microseconds in their time-of-flight apparatus.

v'	0	1	2	3	4	5	6
τ (microseconds)	15.5	13.7	12.2	11.0	9.9	9.1	8.4

This ion transit time, i.e., the time required to travel from the ion source to the center of the reaction region is about the same magnitude (8-9 microseconds) as that in the Langley apparatus. Electronic, vibrational, and rotational transitions are important only when such transitions can take place during the time of the collision. It was shown in the previous section that only vibrational transitions are of importance here.

It has been shown[12] that certain low vibrational levels are most strongly populated by the electron-impact-ionization process. A fraction of the $A^2\pi_u$ state ions entering the analyzer tube will transit the collision region in the same state. The presence of this fraction of undecayed $A^2\pi_u$ state ion can have an effect on observed charge-transfer cross sections. Flannery et al.[12] have shown that the population of the $X^2\Sigma_g^+$ and $A^2\pi_u$ ionic states are in the ratio of approximately 90:10 for electron impact energy of 20 electron volts. Ions formed at this electron energy have two possible reaction paths available in the charge transfer process: A channel where secondary ions are formed in the $X^2\Sigma_g^+$ state and a channel where secondary ions are formed in the $A^2\pi_u$ state. From the analysis of Flannery et al.[12] it is pointed out that the reaction channel where the secondaries are formed in the $A^2\pi_u$ state is an order of magnitude more favorable than the $X^2\Sigma_g^+$ channel. As a result, the contribution to the total charge transfer cross section due to the $A^2\pi_u$ ions would be smaller than the population of this state in the reactant ion beam. It appears that certain excited-state ions can charge transfer less efficiently than ground state ions and may have some influence on the magnitude of cross sections observed. An object of this research has been to probe the relative contributions of excited states in the $N_2^+ + N_2$ reaction.

REFERENCES

1. Utterback, N. G.; and Miller, G. W.: Rev. Sci. Instr., 32, 1101 (1961).

2. Lehrle, R. S.; Parker, J. R.; Robb, J. C.; and Scarborough, J.: Int. J. Mass Spectrom. Ion Phys., 1, 455 (1968).

3. Stebbings, R. F.; Turner, B. R.; and Smith, A. C. H.: J. Chem. Phys., 38, 2277 (1963).

4. Dillon, J. A.; Sheridan, W. F.; and Edwards, H. D.: J. Chem. Phys., 23, 776 (1955).

5. Stebbings, R. F.; Turner, B. R.; and Rutherford, J. A.: J. Geophys. Res., 71, 771 (1966).

6. Homer, J. B.; Lehrle, R. S.; Robb, J. C.; and Thomas, D. W.: Trans. Faraday Soc., 62, 619 (1966).

7. McDowell, M. R. C., ed.: Atomic Collision Process, pp. 847-853, North-Holland Publishing Company, Amsterdam, 1964.

8. McDowell, M. R. C., ed.: op. cit., pp. 854-961.

9. Stebbings, R. F.; Smith, A. C. H.; and Gilbody, H. B.: J. Chem. Phys., 38, 2280 (1963).

10. Nichols, B. J.; and Witteborn, F. C.: NASA Technical Note, D-3265 (1965).

11. Potter, R. F.: J. Chem. Phys., 22, 974 (1954).

12. Flannery, M. R.; Cosby, P. C.; and Moran, T. F.: J. Chem. Phys., 59, 5494 (1973).

13. Leventhal, J. J.; Moran, T. F.; and Friedman, L.: J. Chem. Phys., 46, 4666 (1967).

14. Moran, T. F.; McCann, K. J.; and Flannery, M. R.: J. Chem. Phys., 63, 3857 (1975).

15. Rapp, D.; and Francis, W. E.: J. Chem. Phys., 37, 2631 (1962).

16. Gurnee, E. F.; and Magee, J. L.: J. Chem. Phys., 26, 1237 (1957).

17. Smith, D. L.; and Futrell, J. H.: J. Chem. Phys., 59, 463 (1973).

18. Leventhal, J. J.; and Friedman, L.: J. Chem. Phys., 46, 997 (1967).

19. Dalgarno, A.: Rev. Mod. Phys., 39, 858 (1967).

20. Neimann, H. B.: Rev. Sci. Instrum., 43, 1151 (1972).

21. Turner, B. R.; Rutherford, J. A.; and Stebbings, R. F.: J. Geophys. Res., 71, 4521 (1966).

22. Kaneko, Y.: J. Phy. Soc. Japan, 16, 1587 (1960).

23. Bates, D. R.; and Reid, R. G. H.: Proc. Roy. Soc., A310, 1 (1969).

24. Bates, Dr. R.; and Lynn, N.: Proc. Phys. Soc., A253, 141 (1959)

25. Herzberg, G.: Molecular Spectra and Molecular Structure, D. Van Nostrand Company, Inc., Princeton, N.J., 1950.

26. Mason, E. A.; and Schamp, H. W., Jr.: Ann. Phys., 4, 233 (1958).

27. Mason, E. A.; and Vanderslice, J. T.: J. Chem. Phys., 31, 594 (1959).

28. Hirschfelder, J. O.; Curtis, C. F.; and Bird, R. B.: Molecular Theory of Gases and Liquids, Wiley, New York, 1964; pp. 950-1110.

29. Sato, S.: J. Chem. Phys., 23, 529 (1955).

30. Nicholls, R. W.: J. Res. Natl. Bur. Stand. (U.S.), A65, 451 (1961).

31. Moran, T. F.; and Friedman, L.: J. Chem. Phys., 42, 2391 (1965).

32. Lofthus, A.: "The Molecular Spectrum of Nitrogen," Spectroy. Rept. No. 2, Department of Physics, University of Oslo, Blinden, Norway, 1960.

33. Krupenie, P. H.; and Weissman, S.: J. Chem. Phys., 43, 1529 (1965).

34. Gilmore, F. R.: J. Quant. Spectrosc. Radiat. Transfer, 5, 369 (1965).

35. Henrici, P.: Elements of Numerical Analysis, p. 280, John Wiley and Sons, Inc., New York, N.Y., 1964.

36. Smith, A., "Studies of Charge Transfer in the N_2^+-N_2 System," Ph.D. Dissertation, Va. Pol. Inst. and State Univ., 1977.

37. McDaniel, E. W.: Collision Phenomena in Ionized Gases, p. 340, John Wiley and Sons, Inc., New York, N.Y., 1964.

38. Gosh, S. N.; and Sheridan, W. F.: J. Chem. Phys., 26, 480 (1957).

39. Gustafsson, E.; and Lindholm, E.: Ark. Fysik., 18, 219 (1960).

40. Desequelles, J.; Dufay, M.; and Poulizac, D. C.: Phys. Letters, 27A, 96 (1968).

41. Hesser, J. E.: J. Chem. Phys., 48, 2518 (1968).

42. Holland, R. F.; and Mair, W. B. II: J. Chem. Phys., 56, 5229 (1972).

43. Gray, D. D.: Roberts, T. D.; and Morack, J. L.: J. Chem. Phys., 57, 4190 (1972).

44. Peterson, J. R.; and Moseley, J. T.: J. Chem. Phys., 58, 172 (1973).

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA CR-3307		

4. Title and Subtitle	5. Report Date
THE MULTISTATE IMPACT PARAMETER METHOD FOR MOLECULAR CHARGE EXCHANGE IN NITROGEN	August 1980
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Juliette W. Ioup	
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
Xavier University New Orleans, LA 70125	NSG-1361
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Contractor Report
National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

Langley Technical Monitor: George M. Wood, Jr.

Final Report

16. Abstract

The multistate impact parameter method of Flannery et al. is applied to the calculation of total cross sections for low-energy charge transfer between nitrogen ions and nitrogen molecules. Experimental data showing the relationships between total cross section and ion energy for various pressures and electron ionization energies were obtained by Smith at NASA Langley Research Center. Calculated and experimental cross section values from this work are compared with the experimental and theoretical results of other investigators.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
charge transfer, multistate impact parameter method, nitrogen ion, nitrogen molecule	Unclassified - Unlimited Subject Category 72

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	30	A03

For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1980

END

5-22-81